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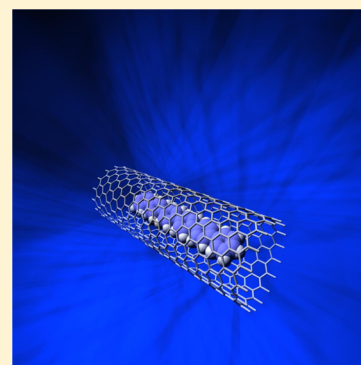
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Evidence of Hybrid Excitons in Weakly Interacting Nanopeapods

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Supporting Information

ABSTRACT: Nanopeapods, consisting of optically active π -conjugated molecules encapsulated inside of the cavity of carbon nanotubes, exhibit efficient photon emission in the visible spectral range. Combining optical experiments with ab initio theory, we show that the puzzling features observed in photoluminescence spectra are of excitonic nature. The subunits though being van der Waals bound are demonstrated to interact in the excited state, giving rise to the formation of hybrid excitons. We rationalize why this many-body effect makes such nanohybrids useful for optoelectronic devices.



SECTION: Spectroscopy, Photochemistry, and Excited States

Single-wall carbon nanotubes exhibit extraordinary physical and mechanical properties, making them attractive for applications in nanodevices. Their usage as photonic components, however, is hampered as they, due to their small band gaps, only emit light in the infrared range of the spectrum. To remedy this shortcoming, optically active molecules (“peas”) have been inserted into the tubes’ cavities (“pods”). In this way, organic–inorganic hybrid nano-objects, so-called nanopeapods, are formed. Several attempts with various organic molecules such as β -carotene, Zn-diphenylporphyrin, or perylene derivatives,^{1–3} inserted in the hollow space of carbon nanotubes have been made. However, these first experiments have not led to light emission, although energy transfer from the molecule to the nanotube was found.¹ Only recently, efficient visible photon emission by carbon nanotubes containing oligothiophenes has been reported.^{4–6} In these systems, the subunits have been shown to interact only through van der Waals forces.⁴ As a consequence, the band structure appears basically as a superposition of the individual electronic states stemming from the respective constituents.⁵ Surprisingly, it is this weakly interacting nanohybrid family that proved to be highly attractive for optoelectronic applications, as demonstrated by a strong photoluminescence signal.

It was immediately proposed⁷ that Kasha’s rule was broken in these nanohybrids. Kasha’s rule states that fluorescence occurs from the lowest-energy excited state, and only a few rare exceptions to it are known.⁸ Because, in nanopeapods, the

lowest states originate from the nanotubes, emission of visible light was expected to be impossible. Hence, the findings by Loi and co-workers,⁴ and later by Okazaki and co-workers⁶ proving the opposite, ask for deeper insight into the radiation processes in such nano-objects. Here, we aim to elucidate the peculiar mechanism behind this physical phenomenon by combining many-body perturbation theory with optical measurements. Using the example of encapsulated sexiphenyl (6P) molecules, we demonstrate that light emission in such systems is facilitated by the interaction of the pea and pod during the excitation process.

The efficient light emission of 6P inside of carbon nanotubes, labeled as 6P@CNT, is demonstrated in Figure 1. In the top panel, photoluminescence (PL), time-resolved PL, and photoluminescence excitation (PLE) spectra of these peapods (light blue solid lines) are depicted. Compared to those of the isolated molecules in solution (dark blue dotted lines), the PL peaks in the same energy range but shows a redistribution of the oscillator strength and a broadening accompanied by a red shift. This observation is analogous to what was found for thiophene-based peapods.⁴ Similarly, the de-excitation time becomes distinctly shorter by encapsulation. While the PL decay of the isolated molecule can be fitted monoexponentially

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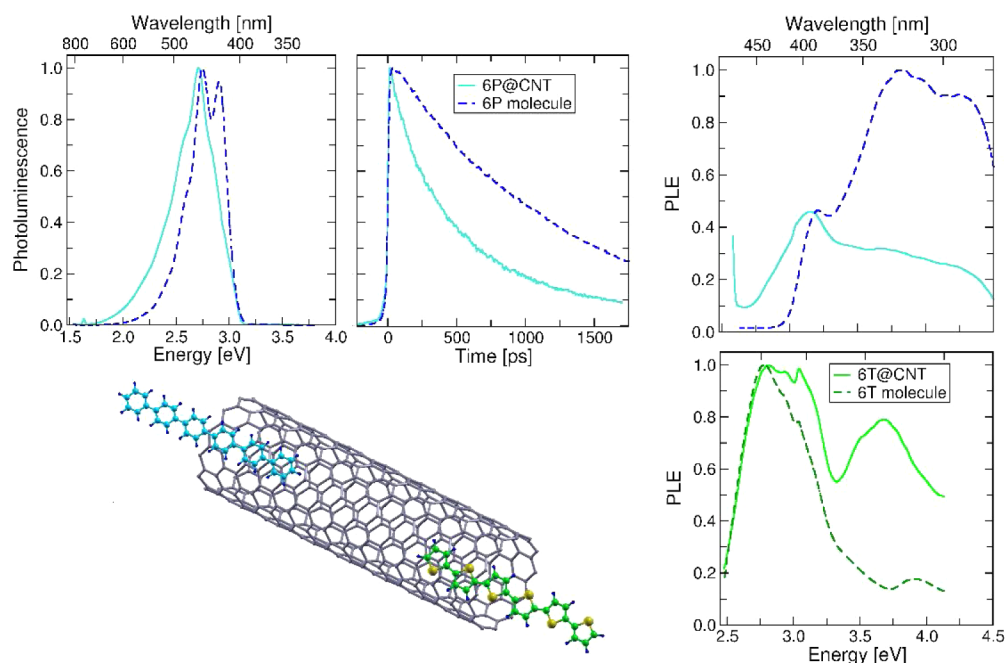


Figure 1. Photoluminescence spectra of light-emitting nanohybrids. (Top) PL, time-resolved PL, and PLE measurements of 6P encapsulated in SWNTs (light blue solid lines) and in solution (dark blue dotted lines). In the PLE spectra, the detection wavelength was 2.48 eV (500 nm). (Bottom) PLE spectra of sexithiophene peapods and sexithiophene molecules in solution recorded with a detection wavelength of 2.25 eV (550 nm). The sketch exemplarily visualizes the encapsulation of molecules in a nanotube. The color code is chosen such that blue is used for 6P and green for sexithiophene for both the molecules as well as spectra.

(as is it typical for isolated molecules) with a lifetime of 1.3 ns, the peapods show a biexponential decay behavior with components $\tau_1 = 55$ ps and $\tau_2 = 730$ ps. The effective lifetime, $\tau_{\text{eff}} = 469$ ps, is calculated using $\tau_{\text{eff}} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$, with A_1 and A_2 being the weights of the components. The reduced lifetime indicates the appearance of additional decay channels.

Ab initio calculations provide a better understanding of these findings. They were performed by many-body perturbation theory on top of self-consistent density functional calculations for the ground state. The quasi-particle band structure was obtained within the G_0W_0 approximation, and the Bethe–Salpeter equation (BSE) was solved to account for excitonic effects. (Computational details are described in the Supporting Information.) In Figure 2, we show the dielectric function of the peapod as well as its isolated constituents. Note that for computational reasons, we replace the oligomer 6P by its infinite analogue poly(*para*-phenylene) (PPP). Although excitonic effects dominate all of the spectra, let us, nevertheless, leave them out for a moment to discuss the situation when electron–hole correlations would be absent. Theory can mimic this situation by reducing the two-particle Hamiltonian to the independent particle approximation (IPA) or, in other words, by “switching off” the Coulomb interaction between the electron and hole. The corresponding results are displayed by light gray areas in Figure 2a. Similar to the ground state, where the subunits do not interact,⁵ we observe that the peapod’s spectrum is merely a superposition of those of the individual subsystems.

The situation entirely turns around when the electron–hole interaction is taken into account as it gives rise to strongly bound excitons. Comparing the results obtained by the two approaches, one can determine the exciton binding energy of the lowest active excitation by the red shift of the

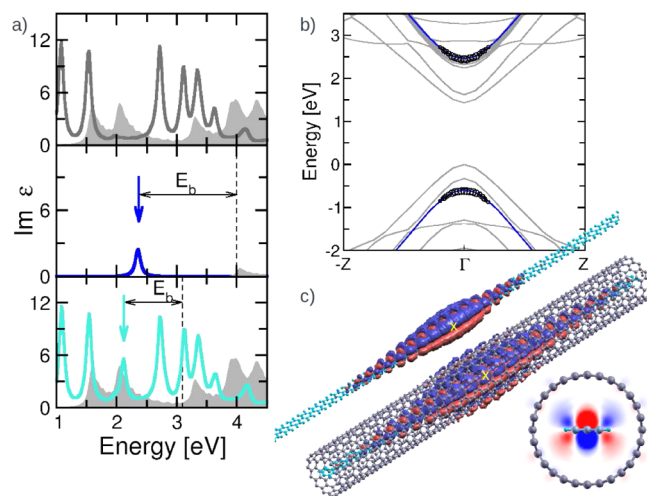


Figure 2. Excitonic spectra and wave functions from many-body perturbation theory. (a) Imaginary part of the frequency-dependent dielectric function for a (14,0) nanotube, poly(*para*-phenylene), and the corresponding peapod, PPP@ (14,0) (from top to bottom). Colored lines (light gray areas) show spectra with (without) electron–hole interaction. Vertical dashed lines and arrows, respectively, indicate the G_0W_0 band gap and the lowest exciton of PPP in the respective environment. (b) G_0W_0 band structure of the peapod. Bands originating from the polymer (nanotube) are specified by the blue (gray) color. Black circles highlight the electronic states involved in the hybrid exciton located at 2.1 eV of the peapod spectrum. Their size corresponds to the weight of the respective contribution. (c) Exciton wave function for the isolated polymer as well as for the hybrid exciton. The pictures show the spatial distribution of the electron with the hole fixed at the site tagged by the yellow crosses. For the latter, also the projection into the plane perpendicular to the tube axis is depicted.

corresponding peak. This amounts to around 1.6 eV for the polymer (Figure 2a, middle panel) and 0.5 eV for the nanotube (Figure 2a, top panel), as already found for similar systems.^{9,10} Likewise, strong excitonic effects have a decisive impact on the peapod's optical spectrum. However, in contrast to the IPA, a simple superposition of the constituents' spectra does not lead to the one computed for the combined system. This finding indicates that the nature of the optical excitations has changed its character by the encapsulation of the molecule.

Generally, the peapod's dielectric function resembles the one of the nanotube, which is responsible for the two lowest-lying peaks below 2 eV as well as most of the features above 2.5 eV. The most striking observation, however, is related to the lowest exciton originating from the molecule, which is found at 2.4 eV when isolated. As this is the key player in view of the desired light-emitting properties, its "disappearance" in the combined system is puzzling and deserves our particular attention. At the same time, a new feature at 2.1 eV shows up in the peapod spectrum. We demonstrate in the following that it is this peak that corresponds to the above-mentioned molecular excitation and is altered through the interaction between the pea and pod.

Valuable insight can be gained by analyzing the electron–hole wave functions. In Figure 2c, this wave function is shown for the lowest-lying exciton of the molecule corresponding to the peak at 2.4 eV in the top panel of Figure 2a as well as for its counterpart in the peapod (peak at 2.1 eV in the lowest panel). In both cases, the position of the hole is fixed in the center of the polymer repeat unit (see the Supporting Information) such that the electron distribution is depicted. The comparison of the two pictures clearly shows that the peapod's exciton is unambiguously derived from that of the molecule but altered in the sense that there is a finite probability for the electron to reside on the tube's circumference. This stronger delocalization of the electron–hole pair is indicative of a weakened Coulomb interaction. It gives rise to a lowering of the exciton binding energy and thus would result in a blue shift of the singlet–exciton peak from 2.3 to 2.7 eV with respect to the band edge.

There is, however, a competitive effect to this blue shift. It is the renormalization of the molecule's band gap from 4.0 to 3.1 eV (dashed vertical lines in Figure 2a) upon encapsulation, which can be traced back to the proximity of PPP to the polarizable surface of the CNT.^{11,12} These two competing effects result in an overall red shift of 0.3 eV in the spectrum in Figure 2a, in excellent agreement with experiments (see Figure 1).

In contrast to the isolated PPP, where this electron–hole pair involves transitions between the highest occupied and the lowest unoccupied orbital of the polymer, in the peapod, electronic bands of both subunits contribute, as evidenced in Figure 2b. It shows the band structure of the peapod, where bands originating from the polymer are marked by blue and those from the nanotube by the gray color. The electronic states involved in this particular exciton are indicated by black symbols. In other words, the original molecular excitation has turned into a hybrid exciton with charge-transfer character opening a perspective toward the peapods' applicability in nanodevices.

Photoluminescence excitation experiments underpin the theoretically obtained picture outlined above. The corresponding spectra are shown in the right panels of Figure 1 for 6P@CNT (top). While PL spectroscopy as depicted in the left panel only probes the molecule in the excited state, the PLE spectrum provides a richer set of information. It reveals which electronic

transitions are involved in the emission process and can thus evidence the presence of hybrid excitons in our nano-objects. Overall, we observe a general broadening and an extreme redistribution of the intensity between the spectral features upon encapsulation of molecules. In particular, the two high-energy features of the 6P spectrum at 4.26 and 3.84 eV show a lower intensity with respect to the feature at 3.21 eV. Most important, however, is that the PLE spectrum of 6P@CNT exhibits the lowest-lying exciton peak at 3.15 eV compared to that in solution at 3.21 eV. This small change reflects the fact that the two above-described competing effects cancel each other nearly completely in this case.

Our calculations are able to explain the direction and magnitude of the exciton peak shift upon encapsulation; a fully quantitative comparison, however, is not possible for three reasons. First, experimental samples consist of a mixture of several tube diameters and chiralities, which largely smears out the peak widths. Moreover, the measurements were performed in solution (see the Supporting Information), which influences the absolute peak positions but should not alter the effect of encapsulation. Second, the measurements were performed for the 6P molecule encapsulated into these nanotubes. It is well-known that the band gaps of oligophenylenes follow a linear trend as a function of the inverse number of repeat units.¹³ Thus, replacing PPP by the 6P is expected to result in a blue shift of about 0.3 eV. The last effect is connected to geometrical considerations. The ground-state geometry of crystalline PPP exhibits an inter-ring torsion angle of about 18° between adjacent molecules. Because the polymer–wall distance in the peapods is very similar to that of the intermolecular distance in bulk, a similar inter-ring torsion angle is to be expected. This is neglected by considering only a one-ring unit cell in the calculation. However, as pointed out by Artacho and co-workers, the polymer undergoes structural changes in the excited state, tending to planarize the polymer chain.¹⁴ Hence, our planar model is well justified. Anyway, addressing the overall effect of molecular length and geometrical considerations, we expect a further blue shift that would move the theoretical result even closer to experiment.

Unfortunately, the absorption spectrum of 6P is at the blue end of the visible spectrum, thus not allowing for an easy investigation at even higher energy. Such an experiment is, however, possible with the analogous samples with thiophene oligomers as peas. The corresponding PLE spectrum of 6T@CNT is displayed in the bottom of Figure 1 together with that of the molecules in solution. The two spectra both show a main peak at 2.79 eV; however, the peapod exhibits a much broader main feature and another peak with an intensity only 20% weaker than the first one at 3.68 eV. This peak is absent in the isolated molecule, where the highest-energy feature is found at 3.91 eV. We interpret this new feature as a hybrid exciton due to the mixed character of transitions involving energy levels of the CNTs as well as of the organic molecules.

In conclusion, we have performed a combined theoretical and experimental study on the mechanism of light emission in optically active nanopeapods consisting of 6P embedded in a single-wall carbon nanotube. Experimentally, we find that the interaction between the pea and pod is characterized by a redistribution of oscillator strength, the appearance of new features in the PLE spectrum (6T@CNT), and a shortening of the PL excitation time. Theory provides the explanation by revealing the coupling of the pea and pod in the excited state. The calculations demonstrate that hybrid excitons are the

essence of the interaction mechanism. These excitons are spatially as well as energetically distributed over both subsystems, giving rise to new features in the optical response of the peapod. This is an important fact as the interplay between the two constituents is a prerequisite for their use in optoelectronic devices. In practice, applying a voltage to the tube would facilitate light emission of the molecule. We believe that this principle applies more generally to weakly interacting hybrid structures, enabling their applicability in photonic devices.

■ ASSOCIATED CONTENT

■ Supporting Information

Computational and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Yanagi, K.; Iakubovskii, K.; Kazaoui, S.; Minami, N.; Maniwa, Y.; Miyata, Y.; Kataura, H. Light-Harvesting Function of β -Carotene Inside Carbon Nanotubes. *Phys. Rev. B* **2006**, *74*, 155420.
- (2) Kataura, H.; Maniwa, Y.; Abe, M.; Fujiwara, A.; Kodama, T.; Kikuchi, K.; Imahori, H.; Misaki, Y.; Suzuki, S.; Achiba, Y. Optical Properties of Fullerene- and Non-Fullerene-Peapods. *Appl. Phys. A: Mater. Sci. Process.* **2002**, *74*, 349–354.
- (3) Fujita, Y.; Brandow, S.; Iijima, S. Formation of Small-Diameter Carbon Nanotubes from PTCDA Arranged Inside the Single-Wall Carbon Nanotubes. *Chem. Phys. Lett.* **2005**, *413*, 410–414.
- (4) Loi, M. A.; Gao, J.; Cordella, F.; Blondeau, P.; Menna, E.; Bártová, B.; Hébert, C.; Lazar, S.; Botton, G.; Milko, M.; Ambrosch-Draxl, C. Encapsulation of Conjugated Oligomers in Single Wall Carbon Nanotubes: Towards Nano-Hybrids for Photonic Devices. *Adv. Mater.* **2010**, *22*, 1635–1639.
- (5) Gao, J.; Blondeau, P.; Salice, P.; Menna, E.; Bártová, B.; Hébert, C.; Leschner, J.; Milko, M.; Ambrosch-Draxl, C.; Loi, M. A. Electronic Interactions between "Pea" and "Pod": The Case of Oligothiophenes Encapsulated in Carbon Nanotubes. *Small* **2011**, *7*, 1807–1815.
- (6) Okazaki, T.; Iizumi, Y.; Okubo, S.; Kataura, H.; Liu, Z.; Suenaga, K.; Tahara, Y.; Yudasaka, M.; Okada, S.; Iijima, S. Coaxially Stacked Coronene Columns Inside Single-Walled Carbon Nanotubes. *Ang. Chem., Int. Ed.* **2011**, *50*, 4853–4857.
- (7) Yanagi, K.; Kataura, H. Carbon Nanotubes: Breaking Kasha's Rule. *Nat. Photonics* **2010**, *4*, 200–201.
- (8) Klan, P.; Wirz, J. *Photochemistry of Organic Compounds*; John Wiley & Sons: New York, 2009; Chapter 2, pp 40–41.
- (9) Bussi, G.; Ruini, A.; Molinari, E.; Caldas, M. J.; Puschnig, P.; Ambrosch-Draxl, C. Interchain Interaction and Davydov Splitting in Polythiophene Crystals: An *Ab Initio* Approach. *Appl. Phys. Lett.* **2002**, *80*, 4118–4120.

(10) Spataru, C. D.; Ismail-Beigi, S.; Benedict, L. X.; Louie, S. G. Excitonic Effects and Optical Spectra of Single-Walled Carbon Nanotubes. *Phys. Rev. Lett.* **2004**, *92*, 077402.

(11) Neaton, J. B.; Hybertsen, M. S.; Louie, S. G. Renormalization of Molecular Electronic Levels at Metal–Molecule Interfaces. *Phys. Rev. Lett.* **2006**, *97*, 216405.

(12) Puschnig, P.; Amiri, P.; Draxl, C. Band Renormalization of a Polymer Physisorbed on Graphene Investigated by Many-Body Perturbation Theory. *Phys. Rev. B* **2012**, *86*, 085107.

(13) Puschnig, P.; Ambrosch-Draxl, C. Density-Functional Study for the Oligomers of Poly(*para*-Phenylene): Band Structures and Dielectric Tensors. *Phys. Rev. B* **1999**, *60*, 7891–7898.

(14) Artacho, E.; Rohlfing, M.; Cote, M.; Haynes, P. D.; Needs, R. J.; Molteni, C. Structural Relaxations in Electronically Excited Poly(*para*-Phenylene). *Phys. Rev. Lett.* **2004**, *93*, 116401.